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AN APPARATUS AND METHOD FOR THE DETERMINATION OF HELIUM IN NATURAL GAS

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BY

C. C. ANDERSON

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AN APPARATUS AND METHOD FOR THE DETERMINATION OF HELIUM IN NATURAL GAS[1]

By C. C. Anderson[2]

INTRODUCTION

While conducting investigations in connection with the helium program of the Bureau of Mines, the Cryogenic Laboratory has improved an apparatus for the rapid and accurate determination of the helium content of natural gas and gaseous mixtures derived from that source. The separation of helium is effected by the use of activated coconut charcoal which, when cooled to liquid-air temperatures, absorbs the nitrogen and other constituents of the gas, leaving the helium in a spectroscopically pure state. This absorptive property of activated charcoal was discovered by Dewar[3] in 1875. Several years later, while conducting their original researches on helium in natural gas, Cady and McFarland employed the charcoal method for the absorption and removal of the common constituents of natural gas and constructed an efficient apparatus in which this operation could be effected.[4] Shortly after initiating the Government's helium activities during the World War period, the Bureau of Mines adopted, with minor modifications, the Cady and McFarland apparatus and method of analysis. Seibel[5] described this modified apparatus and method of procedure as part of a publication on helium-bearing natural gas. Subsequently, the Bureau's apparatus for helium analysis has been simplified and improved to facilitate more rapid and positive operation. The apparatus and method of procedure now being used by the Bureau of Mines Cryogenic Laboratory are described in this paper.

1/ The Bureau of Mines will welcome reprinting of this paper, provided the following footnote acknowledgment is used: "Reprinted from U. S. Bureau of Mines Information Circular 6796."

2/ Associate chemist, U. S. Bureau of Mines Cryogenic Laboratory, Amarillo, Tex.

3/ Dewar, James, Charcoal Vacua: Nature, vol. 12, July 15, 1875, p. 217; The Absorption and Thermal Evolution of Gases Occluded in Charcoal at Low Temperatures: Proc. Roy. Soc., vol. 74, 1904, pp. 122-127.

4/ Cady, H. P. and McFarland, D. F., The Occurrence of Helium in Natural Gas and the Composition of Natural Gas: Jour. Am. Chem. Soc., vol. 29, 1907, pp. 1525-1526.

5/ Rogers, G. S., Helium-Bearing Natural Gas: U. S. Geol. Survey Prof. Paper 121, 1921, pp. 41-42.

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ACKNOWLEDGMENTS

The personnel of the Bureau of Mines Cryogenic Laboratory has improved and brought the helium apparatus described herein to its present state of perfection. The writer's contributions have been of minor importance, and he wishes to give the various members and former members of the laboratory staff full credit for the improvements they have made. He also desires to express his appreciation for suggestions and criticisms offered during the preparation of this paper to the following members of the Petroleum and Natural Gas Division, Bureau of Mines, which now includes the Amarillo Helium Plant and Cryogenic Laboratory: R. A. Cattell, chief engineer; C. W. Seibel, supervising engineer of the Amarillo Helium Plant; W. M. Deaton, chemist-in-charge of the Cryogenic Laboratory; and H. S. Kennedy.

THE ABSORPTION METHOD

The quantitative determination of helium in a gaseous mixture is accomplished by the removal of the other constituents from the sample, either by chemical or physical means, leaving only the helium which can be measured directly. Chemical methods, when applied to natural gas, require the burning of the hydrocarbons in oxygen, the absorption of the resulting carbon dioxide in a caustic solution, the removal of the excess oxygen in a suitable solution such as an alkaline pyrogallate, and the elimination of nitrogen by sparking or by combination with hot calcium or magnesium. Such procedures are very slow and tedious compared with the physical method which employs the absorptive property of activated charcoal to effect the separation of the other constituents from the helium.

When cooled to liquid-air temperatures, activated cocoanut charcoal absorbs large volumes of the principal constituents of natural gas, such as nitrogen, methane, other gases of the hydrocarbon series, carbon dioxide, and oxygen, if the latter is present in the sample. The thousands of analyses made in the Cryogenic Laboratory indicate that in natural gases of this country hydrogen and neon are either absent or occur in such small percentages as to be absorbed readily by the quantity of charcoal usually employed. Claude[6] found that 10.5 cubic centimeters of hydrogen was absorbed by 100 grams of coconut charcoal at a pressure of 0.0060 millimeter of mercury and a temperature of -195.5°C. For neon his researches did not extend to the very low pressure ranges employed in the method being described. Pentcheff,[7] experimenting with a small quantity of coconut charcoal and small volumes of gas, did not detect a loss of neon by absorption at very low pressures. Further study of the absorption of neon by coconut charcoal at liquid-air temperatures has been made by the writer. Air was used as the source of neon in these experiments, and the volumes of absorbed neon were computed by using Watson's[8] value of 1 volume of neon to

6/ Claude, G., Sur l'absorption des gaz par le charbon aux basses temperatures: Compt. rend., vol. 158, 1914, p. 861.

7/ Pentcheff, N. P., Sur la determination quantitative du neon dans les gas naturels; Compt. rend., vol. 189, 1929, p. 323.

8/ Watson, H., The Densities and Molecular Weights of Neon and Helium: Trans. Chem. Soc., vol. 97, 1910, p. 810.

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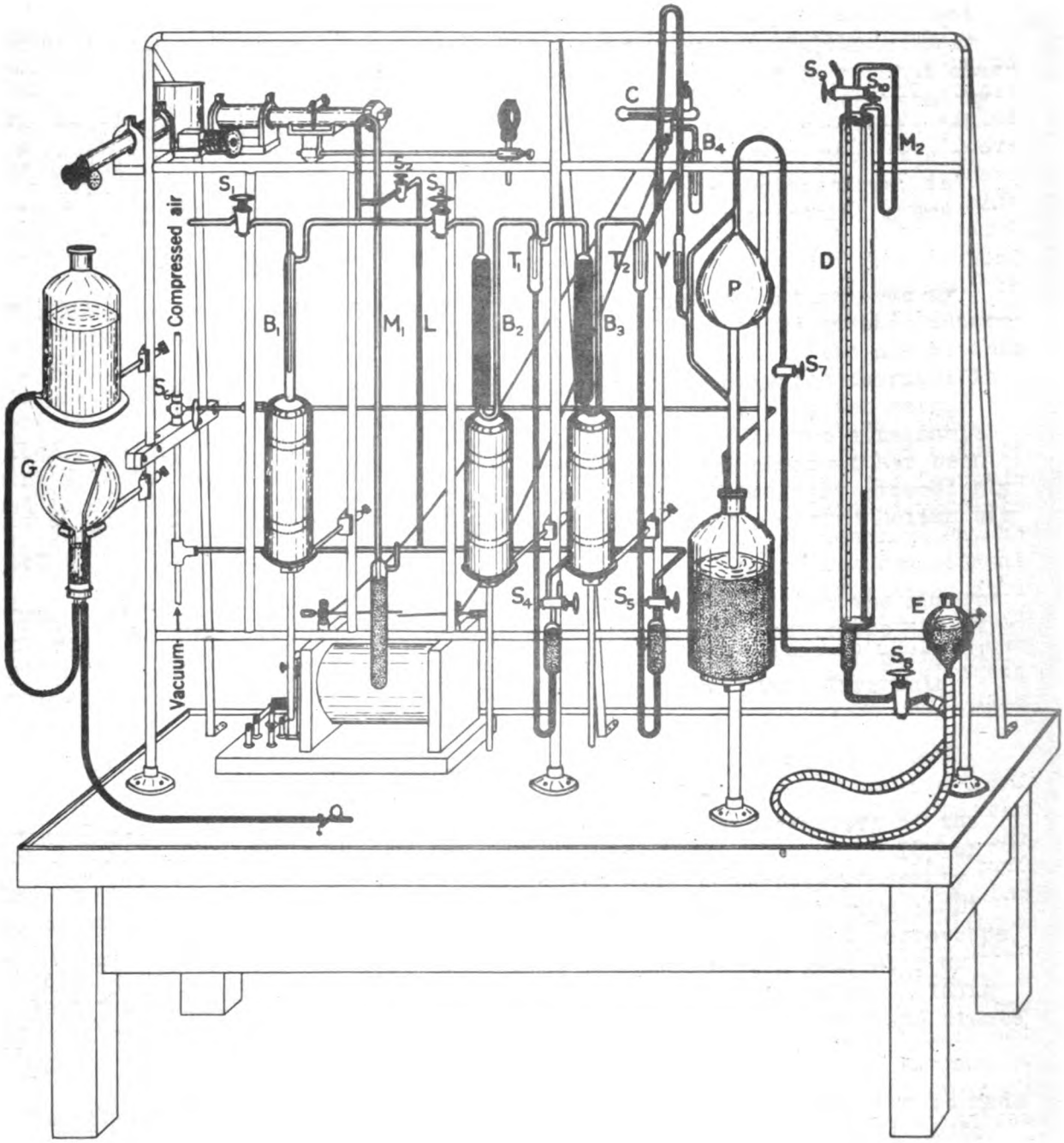

Figure 1.—Apparatus for separation and measurement of helium.

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55,000 volumes of the atmosphere. At liquid-air temperatures and a pressure of approximately 0.0057 millimeter of mercury the absorption of neon was not greater than 0.06 cubic centimeter per 100 grams of charcoal. Although only small volumes of hydrogen and practically no neon are absorbed by coconut charcoal at liquid-air temperatures, spectrum analysis of the helium separated by the absorption method from natural-gas samples analyzed in the Cryogenic Laboratory has shown only minute traces of either of these gases. Thus, the absorption method, employing coconut charcoal at liquid-air temperatures, is applicable to the determination of the helium content of the natural gases ordinarily found in the United States.

The complete absorption of the various constituents of natural gas by charcoal raises the question of partial retention of the helium by this material. Such a partial absorption would be a serious objection to the use of this method. Leduc[9] found that the absorption of helium in activated charcoal is proportional to the pressure. Upon completion of an analysis by the method described, the apparatus has been evacuated to the highest degree attainable by using a Töpler mercury pump. Thus, the pressure on the charcoal has been reduced practically to zero and the absorption of helium should be exceedingly small. This problem was investigated by Kennedy[10] and no absorbed helium was detected under the high-vacuum conditions mentioned.

Thus activated coconut charcoal is an excellent material for the absorption or removal of the various constituents of natural gas and leaves all of the helium for withdrawal and measurement. The charcoal-absorption principle is employed in the helium apparatus used by the Bureau of Mines Cryogenic Laboratory.

DESCRIPTION OF APPARATUS

The apparatus for separation and measurement of helium consists of the following principal parts: A condensation tube, 2 charcoal tubes, a Töpler mercury pump, and a burette. All of these parts and the necessary mercury traps, stopcocks, and manometer are welded together, forming a vacuum-tight apparatus, as shown in figure 1. Accessory equipment includes a spectroscope, spark coil, 6-volt storage battery, a balance for weighing, a gasometer or equivalent for holding the sample before analysis, vacuum flasks for holding liquid air, and pumps or other devices for supplying compressed air and create a vacuum to operate the Töpler mercury pump.

The condensation tube B_1 is approximately 20 centimeters long and is made of suitable size glass tubing, such as 16-millimeter outside diameter, into which an inlet tube of about 7-millimeter outside diameter is sealed. The construction is such that a gas sample, entering the apparatus through stopcock S_1,

9/ Leduc, M. A., Densité et masse atomique du neon: Compt. rend., vol. 158, 1914, p. 864.

10/ Kennedy, H. S., The Absorption of Helium in Charcoal at Liquid-Air Temperatures and Low Pressures: Unpublished thesis on file at the George Washington University Library.

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passes through the inlet tube nearly to the bottom of the condensation tube then rises in close contact with the outer wall to the outlet. One precaution in making this condensation tube is to allow ample space between the end of the inlet tube and the bottom for the collection of liquids.

Between the condensation tube B_1 and the first charcoal tube B_2 is an open manometer M_1, an auxiliary line L with stopcock S_2, and stopcock S_3. By means of the manometer M_1 the pressure in the condensation tube can be observed at any time. The auxiliary line L connects the apparatus to the main vacuum line and is used only during the preliminary evacuation of the tubes and Töpler pump head. Stopcock S_2 closes the line at the completion of this preliminary step. Stopcock S_3 is used to shut off the condensation tube B_1 from the rest of the system when admitting a sample. Since gases pass through this stopcock under high-vacuum conditions, its bore should be large to facilitate rapid pumping.

The charcoal tubes B_2 and B_3 are made of 24-millimeter outside-diameter glass tubing and are approximately 22 centimeters in length. They are constructed so that the gas leaves at the lower ends, thus insuring good contact with charcoal at liquid-air temperatures. The tubes are filled with activated coconut charcoal. Powdery charcoal should be excluded since it plugs the spaces between the larger grains, increases the resistance to gas flow, and prolongs the pumping operation. Satisfactory service has been given by coconut charcoal of 8- to 14-mesh size and having a chlorpicrin tube test of 40 minutes.[11] After filling, the ends of the tubes are plugged loosely with wire gauze or glass wool to hold this material. Tubes of the size described hold approximately 35 grams of charcoal each. Care should be taken in bending the exit tubes so that the charcoal bulbs will fit loosely in the wide-mouthed vacuum flasks selected for the liquid-air containers.

Between the charcoal tubes B_2 and B_3 and beyond the latter tube the apparatus is provided with mercury-trap seals T_1 and T_2. In making an analysis these traps are used in closing off parts of the system, as described later. The mercury reservoirs for these traps are placed approximately 10 centimeters less than a barometric height below the inlet tubes of the traps and are equipped with three-way stopcocks S_4 and S_5 for controlling the mercury levels. By opening the reservoirs to atmospheric pressure, the traps are closed and by turning the stopcocks to the vacuum line, they are opened again. These traps, being free from leakage troubles and offering very little resistance to the flow of gases when open, are used instead of stopcocks.

The spectrum tube C is teed off of the line leading from the last mercury trap T_2 to the Töpler pump. A condensation tube B_4, smaller than tube B_1 but similar in design, is placed in the spectrum tube line. When immersed in liquid air, tube B_4 serves to condense and hold water vapor left in the system before starting the first analysis and mercury vapor, thus keeping all but mere traces of these objectionable vapors from the spectrum tube.

11/ Fieldner, A. C., Oberfell, G. G., Teague, M. C., and Lawrence, J. N., Methods of Testing Gas Masks and Absorbents: Ind. and Eng. Chem., vol. 11, 1919, pp. 519-540.

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Any one of several types of spectrum tubes can be used. The spectrum tube, used on the apparatus being described, is constructed so that the light passes through a capillary tube and can be viewed from either the side or end. The gas in the spectrum tube is excited by means of a spark coil, operated by a 6-volt storage battery. The coil is adjusted to give a spark about 3 centimeters long in air. Care must be taken to insulate the wires carrying the high-potential current to the spectrum tube to avoid shorting to the equipment rack or puncturing the glass apparatus.

The helium, after absorption of the other constituents of the sample, is removed from parts of the apparatus thus far described for measurement by means of the Töpler mercury pump P. This pump has a pear-shaped chamber or pump head of about 1-liter capacity. This pump head, placed in an upright position, has an advantage over the inclined Antropoff[12] type in that it is less likely to trap gas on the walls of the chamber. A glass check valve V prevents the mercury from flowing backward into the spectrum and charcoal tubes. A 2-liter acid bottle is used as a mercury reservoir for the pump. Since this bottle is subjected alternately to vacuum and pressure conditions, it is shielded by a jacket of transparent plastic material, not shown in figure 1, to protect the operator in case of breakage.

The Töpler pump requires a supply of compressed air of about 18 pounds and a source of vacuum. The latter can be produced by operating a rotary-type oil pump or a good water-jet pump. The pressure or vacuum is applied to the mercury reservoir of the Töpler pump by means of the four-way stopcock S_6, operated by hand.

This four-way stopcock can be conveniently made from an ordinary two-way brass cock. A small hole is drilled through the body of the cock so that the plug will be in an open position at each 90° of revolution. The plug of the cock is modified by closing one end of the bore; drilling a hole through the handle, stem, and core to the bore; and soldering a copper tube in this hole. The copper tube is connected to the line leading to the mercury reservoir by a slip joint which can easily be made by substituting a soft, fibrous packing material for one of the cones in a brass compression-union fitting used to make the connection.

The Töpler pump delivers the helium through capillary glass tubing to the burette D for measurement. The capacity of this burette is 20 cubic centimeters and the calibrated part is approximately 1 meter long. The burette is graduated into 0.05-cubic-centimeter divisions, and readings can easily be estimated to the nearest 0.01 cubic centimeter. A water jacket for maintaining a constant temperature surrounds the burette and auxiliary tube. The latter compensates for changes in barometric pressure during analysis.

12/ Antropoff, Andreas von, Experimentelle Untersuchung Über Die Loslichkeit Der Edelgase in Flussigkeiten: Electrochem. Ztschr., vol. 25, 1919, p. 270.

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For rapid analysis, glass tubing of ample size should be used to connect the various pieces of apparatus. The Cryogenic Laboratory uses 7-millimeter outside-diameter tubing of medium wall thickness for this purpose. The capillary tubing used to join the Töpler pump and burette has a 2-millimeter bore.

Only the best quality of glass stopcocks should be used as the apparatus operates under high-vacuum conditions. The various stopcocks should be large. The bores of the plugs should be oblique so that gas cannot leak around the plugs, following the streaks in the grease. A good stopcock when greased properly should be perfectly clear and show no streaks or air bubbles. Streaks are difficult to avoid unless the stopcocks are cleaned and lubricated frequently.

A grease for high-vacuum work should have a low vapor pressure, lubricate smoothly the ground surfaces of the stopcock, and have sufficient body to stay in place, thus preventing the glass surfaces from touching and sticking. Greases can be purchased from chemical-supply companies or made in the laboratory from unvulcanized rubber, vaseline, and paraffin.13/

MODIFICATIONS OF THE APPARATUS

Samples of natural gas, collected in connection with the Bureau of Mines survey of helium resources, are analyzed in an apparatus constructed according to the foregoing description. This apparatus is somewhat elaborate in order to handle, daily, a large number of samples having widely varying compositions. If only a few samples of more or less known composition are to be tested at a time the apparatus can be simplified.

Since there is always the possibility of finding other rare gases associated with the helium in the samples analyzed in connection with the helium-resource survey, a wave-length spectrometer is used so that these gases might be identified. If the analyst is interested only in testing the purity of the helium in the apparatus, a small hand spectroscope will satisfactorily serve the purpose. Likewise a smaller spark coil will be satisfactory in most instances.

The charcoal tubes of the helium apparatus, as shown in figure 1, will handle easily ten 1-liter samples of natural gas without becoming fouled. If only three or four samples are to be analyzed during the day the charcoal tube B_3 and trap T_2 could be eliminated.

If samples containing 10 percent or more of helium are to be analyzed the apparatus should be modified slightly for satisfactory operation. A burette of 100 cubic centimeters capacity should be substituted for the one described. It is convenient to add an auxiliary line, connecting the top of this burette and the condensation tube B_1. With this addition, samples can be measured accurately in the burette and transferred to the condensation tube without danger of

13/ Shepherd, Martin, and Ledig, P. G., Rubber Stopcock Lubricants for High-Vacuum and Other Uses: Ind. and Eng. Chem., vol. 19, 1927, pp. 1059-1061.

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losing part of the gas. Large bore stopcocks, similar to S_3, should be substituted for mercury traps T_1 and T_2 when the samples contain high percentages of helium as these traps are satisfactory for holding only small differences of pressure.

The Töpler mercury pump, as described, operates very satisfactorily; however, it can be modified to operate manually or automatically. If the laboratory is not provided with compressed air and vacuum equipment, the Töpler pump and traps T_1 and T_2 can be modified for manual operation of the mercury reservoirs. Porter[14] has described an automatic Töpler pump which will work satisfactorily in laboratories having compressed air, vacuum, and direct current. A Sprengel pump may be substituted for the Töpler pump. While it has the advantage of requiring very little attention during the pumping period, the Sprengel pump has the disadvantage of very much slower operation.

PROCEDURE FOR ANALYSIS

Before the preliminary evacuation of the apparatus is started all of the stopcocks should be cleaned properly, lubricated, and turned in the correct positions as follows: S_1 closed, S_2 open, S_3 open, S_4 and S_5 closed with their respective mercury traps T_1 and T_2 open, S_7 open, S_8 open, S_9 open to the atmosphere, and S_6 open to the vacuum line. The auxiliary vacuum pump is then started and the apparatus preliminarily evacuated, the pressure in the system being noted by manometer M_1. If the charcoal is not dry, the tubes containing it are heated to 200°C. by means of cylindrically shaped electrical heaters which can be made in the laboratory. After the moisture is driven off the heaters are removed from the charcoal tubes, and stopcock S_2 is closed. Usually it is not necessary to dry the charcoal tubes at the beginning of each day's operation.

While the charcoal tubes are cooling, a small vacuum flask of liquid air is placed around the condensation tube B_4, and the apparatus is further evacuated by taking 3 or 4 strokes with the Töpler mercury pump. To operate the pump, stopcock S_6 is turned 90° from the vacuum position thus opening the mercury reservoir to atmospheric pressure. Mercury rises into the pump head, trapping a quantity of gas. By turning stopcock S_6 another 90°, compressed air enters the reservoir, and the mercury, continuing to rise, forces the gas from the pump head into the burette D from which it passes to the atmosphere through the open stopcock S_9. To prevent the flow of too much mercury into the burette system, stopcock S_7 may be opened before and closed after each delivery of gas from the pump. After forcing the gas into the burette, stopcock S_6 is turned backward 90° and the air pressure in the mercury reservoir released. The stopcock is then turned to throw a vacuum on the reservoir, withdrawing the mercury from the pump head and thus completing the cycle of operation or stroke of the pump.

14/ Porter, Frank, An Automatic Töpler Pump: Ind. and Eng. Chem., vol. 16, 1924, p. 731.

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When the charcoal tubes B_2 and B_3 have cooled to room temperature, they and the condensation tube B_1 are immersed in liquid air. In a few minutes the activated charcoal absorbs the remaining gas in the system. This absorption is complete when the spectrum tube C fails to light and/or the Töpler pump ceases to deliver gas to the burette. This completes the preliminary preparation of the apparatus for analytical work.

The next step in the procedure is to fill the sampling flask G with gas from the container holding the sample. The method used in making this transfer will depend upon the type of container and upon the pressure of the contained gas. In general, the methods may be divided into two groups: One for samples under such small pressures or even slight vacuums that the gas must be withdrawn from the container by water displacement and the other for samples under sufficient positive pressure that the sampling flask can be filled merely by releasing gas from the container. Samples of the first group are usually contained in glass bottles or light-weight sampling cylinders, while samples of the second group are confined in steel cylinders.

Before the transfer of gas from the container is begun the sampling flask and inlet rubber tube must be filled completely with water to expel any remaining gas from the previous sample. This is done by elevating the aspirator bottle above the sampling flask and opening the pinch clamp until a steady stream of water flows from the inlet tube.

The method of transferring gas from a glass bottle is given as a typical example for samples of the first group. The bottle containing the sample is inverted in a trough of water, care being taken always to hold the mouth of the bottle below the surface of the water to avoid contaminating the sample with air. While the bottle is in this position the stopper is removed and the inlet rubber tube of the sampling flask is inserted into the bottle. The aspirator bottle is then placed below the sampling flask and the pinch clamp on the inlet rubber tube is opened so that water flows from the flask to the aspirator bottle, drawing a gas sample into the flask from the inverted container. After the transfer the pinch clamp is closed, and the aspirator bottle is raised to place a slight pressure on the gas in the sampling flask, thus avoiding the possibility of contamination with air if the pinch clamp does not hold perfectly. Slight modifications may be made in this method to meet the conditions arising from the use of cylinders or special-type containers.

For the second group, that is, samples under sufficient positive pressure to fill the flask, the method of transfer is as follows: A suitable fitting or adaptor is attached to the valve of the gas cylinder so that the inlet rubber tube of the sampling flask can be connected to the cylinder. This adaptor should include a needle valve to control the rate of flow of gas properly in case the sample is under more than a few pounds pressure. After flushing the adaptor with gas from the cylinder to expel the air from it the inlet rubber tube is attached and the pinch clamp is released. Then by careful operation of the cylinder valve or needle valve, as the case may be, the sampling flask is filled with gas. After filling the flask, the needle valve or the cylinder valve is closed, and the pinch clamp is reset on the rubber tube.

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Usually some water remains in the inlet rubber tube after the transfer and must be removed to avoid a freeze-up while making the analysis. A convenient way of doing this is to pinch off the open end of the tube, move the pinch clamp to a point near the sampling flask, and then, while holding the tube above the pinch clamp in one hand, to remove completely the gas and water from the pinch clamp to the end of the tube by a stripping action with the other hand. At the completion of this movement the end of the rubber tube should remain pinched off to exclude air until the pinch clamp is moved back to within 1 or 2 inches of the open end.

After the inlet rubber tube is freed of water the sampling flask and aspirator bottle are leveled so that the gas sample will be at atmospheric pressure, and a pinch clamp is placed on the connecting rubber tube to keep the gas under this pressure. The flask holding the sample is then weighed to the nearest gram on a balance of suitable capacity and the weight recorded. The sampling flask must be placed on the balance pan in the same position for each weighing, and only the same length of connecting rubber tube must be permitted to swing from the pan if weighings are to be duplicated with reasonable accuracy.

At this point, the burette is prepared for the analysis. Stopcock S_{10} is opened, S_7 closed, and S_9 turned so that the burette is opened to the manometer M_2. The water in the manometer is then leveled by use of the leveling bulb E, and stopcock S_9 is turned to close off the manometer. Stopcock S_{10} is closed and remains in this position throughout the remainder of the analysis. The interval between the adjustment of the volume of the gas sample to atmospheric pressure and the closing of stopcock S_{10}, after the water in the manometer is leveled, should be as short as possible since the volumes of gas before and after absorption are compared without taking into account any changes in barometric pressure during this interval; that is, the pressure of the helium measured in the burette is adjusted to equal that in the compensating tube which represents conditions at the time stopcock S_{10} was closed. Unless gas samples contain large percentages of carbon dioxide or hydrogen sulphide they are confined in a gasometer containing water and are saturated with water vapor. The helium leaving the charcoal tubes is dry and must be saturated with water vapor in the burette before measurement for conditions to be comparable with those of the original sample. The compensating tube contains a small volume of water, and the walls of the burette are moistened to establish that condition. After this is done, the leveling bulb E is raised to expel most of the water and all of the air. Enough moisture will cling to the walls of the burette to saturate the helium pumped into it. Stopcock S_9 is then closed and the leveling bulb lowered, producing a reduced pressure in the burette and thus making it ready for the introduction and measurement of the helium.

Stopcocks S_4 and S_5 are carefully opened to the atmosphere, allowing mercury to close the inlets of traps T_1 and T_2, and the stopcocks are then closed. Stopcock S_3 is closed, and the entire apparatus is ready to receive the gas sample.

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The inlet tube of the sampling flask G is connected to the apparatus, the pinch clamps are removed, and the stopcock S_1 is opened a slight amount to admit a small flow of gas into the condensation tube B_1. At liquid-air temperatures, water vapor, carbon dioxide, ethane, and the heavier hydrocarbon gases are condensed in this tube. Moreover, part of the methane is liquefied. Before atmospheric pressure is reached in tube B_1, shown by manometer M_1, stopcock S_1 is closed. Stopcock S_3 is slowly opened and the gaseous mixture, consisting of helium, oxygen, nitrogen, and the methane not condensed in the first tube, passes into the charcoal tube B_2 where all of the gases except the helium are absorbed. This restores a partial vacuum in the condensation tube, and stopcock S_3 is closed. This process is repeated until all of the sample, approximately 1 liter, has been taken into the apparatus.

The mercury trap T_1 is opened by slowly turning stopcock S_4 to the vacuum and then closing the stopcock after the mercury level falls below the inlet tube of the trap. This admits gas to the second charcoal tube. The apparatus is allowed to stand for 3 minutes to give ample time for the complete absorption of the gases. A depression of the mercury level in the inlet tube of trap T_2 indicates the presence of helium in the sample.

While the apparatus is standing, the sampling flask, if not completely emptied of gas, is again leveled to establish atmospheric pressure in the flask, and the latter is weighed. The interval between this leveling operation, if gas remains in the flask, and the balancing of the original sample should be as short as possible to minimize the effect of changing barometric pressure. The difference in the two weighings is the amount of water which displaced the gas sample. This difference in weight, expressed in grams, may be assumed to be equal to the volume of the sample in cubic centimeters. For gases containing more than 3 percent of helium it is advisable to measure the sample in a burette or by some other method which is more accurate than the procedure described.

The apparatus beyond the mercury trap T_2 is tested for possible leaks, first, by exciting the spectrum tube and, secondly, by taking a stroke with the Töpler pump. If the spectrum tube fails to glow and the pump delivers no gas, the analysis can proceed. The pump head is left full of mercury after this test so as to reduce the volume to be occupied by the helium, resulting in a higher pressure for testing in the spectrum tube C.

After the 3-minute absorption period, the mercury trap T_2 is opened, and the spectrum tube is again excited. The color of the light emitted by pure helium depends upon the pressure in the spectrum tube, changing from orange-yellow to green with decreasing pressure. Nitrogen, the most likely impurity, produces a purplish coloration. If the light from the tube is passed through a spectroscope, the helium spectrum[15] presents a series of lines ranging from red to violet. The number of these lines depends upon several factors, one of

15/ Briscoe, H. V. A., The Enert Gases: Textbook of Inorganic Chemistry, ed. by Friend, J. Newton, London, 1919, vol. 1, pt. II, pl. facing p. 313.

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which is the pressure in the spectrum tube. Other conditions remaining constant, diminution of pressure reduced the number of lines, the double yellow line D_3 being the only line visible at very low pressures. The presence of impurities in the gas can be determined readily by use of the spectroscope. Often a faint hydrogen line and a few mercury lines can be seen in the helium spectrum. These are due to traces of water and mercury vapors not removed by condensation tube B_4 and may be disregarded.

If the gas is found spectroscopically to be pure helium, except for traces of water and mercury vapors, the pumping operation previously described is started. Since the upper portion of the burette is under a barometric vacuum, care must be taken to deliver the first gas into it slowly to avoid hammering and possible breakage of the burette. After this precaution has been observed, the pumping is continued and the spectrum tube excited from time to time. As the pressure decreases, the orange-yellow glow changes to green; this is followed by cathode rays and, finally, a black tube. After the black spectrum tube is obtained, pumping is continued for 3 or 4 strokes, or until no more gas is delivered to the burette.

Upon completion of the pumping operation stopcock S_7 is closed, and the volume of helium in the burette is ready for the measuring operation. Leveling bulb E is raised until the pressure of the gas in the burette is approximately equal to atmospheric pressure. Stopcock S_9 is turned carefully to connect the burette with the manometer M_2, and the latter is leveled by slowly raising or lowering bulb E. Stopcock S_8 is then closed and the leveling bulb lowered. The volume of helium in the burette is read, the value being recorded to the nearest 0.01 cubic centimeter.

The volumes before and after absorption are directly comparable without correcting for changes of barometric pressure, temperature, or vapor pressure of water. The water jacket keeps the burette temperature close enough to the temperature at which the gas sample was measured that differences in the latter two variables are small enough to be disregarded. As previously stated, the burette unit compensates for changes in barometric pressure. Thus the percentage of helium in the sample can be computed directly by the following formula:

$$\text{Percentage of helium} = \frac{\text{burette reading in cubic centimeters}}{\text{volume of sample in cubic centimeters}} \times 100.$$

Analyses are reported to the nearest 0.01 percent by the Bureau of Mines Cryogenic Laboratory. Samples showing spectroscopic helium, but not a measurable quantity, are reported as having traces of this element. Samples failing to show spectroscopic amounts are reported as having no helium. The apparatus described in this paper shows spectroscopically the presence of 0.05 cubic centimeter of helium. Samples having less than this amount per liter (0.005 percent) would be reported as having no helium, and samples having 0.005 to 0.007 percent are recorded as having traces.

After becoming familiar with the apparatus, an analyst can complete determinations in 15 to 30 minutes, depending upon the volume of helium to be pumped out of the apparatus, and with ordinary care results can be duplicated within close ranges. For samples having 1 percent or less of helium, check determinations should not vary more than 0.01 percent. Check results for samples having from 1 to 2 percent helium should be within $\pm$0.01 percent.

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